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(54) **Polymer blend.**

(57) A polymer blend useful as a binder in an aqueous coating composition containing no coalescent is provided. The polymer blend comprises from about 20 to about 60 weight percent of a hard emulsion polymer, having a glass transition temperature greater than about room temperature, and from about 80 to about 40 weight percent of a soft emulsion polymer, having a glass transition temperature less than about 20°C.

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This invention relates to a blend of emulsion polymers useful as a film forming binder component in an aqueous coating composition which does not require the presence of volatile organic solvents. More particularly, the invention is directed to the selection of at least two emulsion polymers, having different glass transition temperatures, in certain selected weight ratios; when blended together these permit the formulation of an aqueous coating composition having good film properties without the use of a coalescent.

Aqueous based coatings, such as for example latex or emulsion polymer containing paints, constitute a significant segment of all coatings in use today. Aqueous based coatings offer the advantages of being generally easier to use than conventional oil based coatings, such as for example alkyd paints, and contain fewer undesirable volatile organic solvents. Formulators of aqueous based coatings desire to match or improve upon the performance properties of alkyd-based coatings including their hardness and gloss characteristics.

The glass transition temperature ("T_g") of a polymer is an inherent physical property of the monomer or monomers used to make the polymer. The T_g of a polymer determines the relative hardness or softness of the polymer. The higher the polymer's T_g the harder the polymer is, and the lower the polymer's T_g the softer. The T_g of a polymer determines both the physical characteristics of a film formed from a coating composition containing the polymer and also the minimum temperature at which the coating composition containing the polymer can be applied to a substrate to form a film. For example, in the case of a pigmented architectural coating, two important physical characteristics of the coating are its hardness and its desired degree of gloss. The hardness of a pigmented coating is a function of both the T_g of the polymeric binder and the amount of the pigment used in thee coating composition. Coatings having a high degree of gloss typically contain relatively lower concentrations of pigment than less glossy coatings and, therefore, the contribution of the polymeric binder to the final hardness of the coating is more important than in less glossy coatings. Increasing the T_g of the polymeric binder used in a coating will increase both the gloss and the hardness of the final coating. However, if the T_g of the polymer, selected to provide the coating with the desired high degree of gloss or hardness, is above the minimum temperature required for the coating to form a film, hereinafter referred to as the "Minimum Film Formation Temperature" (or "MFT") a dilemma is created. If the polymer Tg is selected for its ability to contribute hardness to the coating, but the coating will not form a film at the temperatures at which it is to be applied, the coating formulation is not useful regardless of the desirability of the film properties which could be achieved if the coating were to be applied at a temperature equal to or above the minimum film formation temperature. Likewise, if the polymer is selected solely on its ability to form a good film at low temperatures, the coating will form a film at the temperature at which it is to be applied, but the film thus formed will not necessarily have the desired physical properties.

The conventional way which this problem has been solved by aqueous coating formulators is to utilize a coatings binder polymer which will yield the physical properties which are desired, and to address the film formation problem of the polymer separately. This is accomplished through the incorporation of additives in the coating formulation. These additives act by effectively reducing the apparent T_g of the polymer thereby permitting the coating to form a useful film at a temperature below the real T_g of the polymer. The additives which have been selected by aqueous coating formulators for this purpose are conventional volatile organic solvents. The volatile organic solvent additive acts as a plasticizer for the polymeric binder, solubilizing the polymer and reducing the apparent T_g. This apparent reduction in the polymer's T_g permits the formulator to form a film in a reasonable amount of time at a temperature at which the polymer would ordinarily not form a film while at the same time preserving the desired physical properties of the film so formed. The physical properties of the film are preserved because after the coating is applied to a substrate, the coalescent evaporates from the film as the film dries. Thus a film can be formed by the assistance of the coalescent additive without concern to the polymeric binder's real T_g. Coalescents, such as for example 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol), are typically employed in coating formulations at concentrations of from about 3 to about 20 percent by weight on weight of the polymeric binder solids. The concentration of the coalescent typically increases within this range as the desired degree of gloss of the coating increases.

While this has been a very useful way to solve the problem associated with obtaining certain desired film properties with polymers of high T_g which do not readily form films at desired application temperatures, this solution has created another problem. This new problem is associated with the evaporation of the organic solvent additives into the atmosphere. In addition to the unpleasant odor associated with such organic solvents, there is a growing concern about the potentially adverse environmental and health effects of many of them. Since latex coatings have been developed in the first instance for use in aqueous based coatings as an improvement over oil based coatings containing volatile organic solvents, it is an object of water based coatings formulators to further reduce or eliminate the presence of such volatile organic solvents in aqueous based coatings.

Thus it has become desirable to develop a polymeric binder for use in aqueous based coatings which does not require a volatile organic solvent coalescent, but which also does not reduce the physical properties of the

aqueous coating or severely increase its cost of manufacture.

Accordingly the present invention provides a film forming polymeric binder comprising a blend of at least one hard emulsion polymer having a glass transition temperature (T_g) greater than 20°C, preferably from 25 to 65°C, and at least one soft emulsion polymer having a T_g less than 20°C, preferably from 10°C to -5°C, wherein said blend comprises from 20 to 60, preferably from 20 to 40 weight percent of said hard emulsion polymer and from 80 to 40, preferably from 80 to 60 weight percent of said soft emulsion polymer.

In a further aspect the invention provides an aqueous coating composition containing a binder as defined above.

The polymer blend of the invention is particularly useful in aqueous coating compositions which can be applied at low temperatures while providing good block resistance, such as for example interior semi-gloss paints.

It has been found that blending at least one relatively soft emulsion polymer with at least one relatively hard emulsion polymer in selected weight ratios is an effective method for producing a polymeric binder useful in aqueous coating compositions which does not require the presence of volatile organic solvent coalescent.

The present invention derives from the understanding of the relationship between the glass transition temperature of emulsion polymers and the minimum film formation temperature of coatings.

The minimum film formation temperature of a coating is determined experimentally as by using an apparatus described by T.F. Protzman and G.L. Brown in J.Appl. Polymer Sc., 4, 81 (1960). This apparatus is essentially an aluminum slab in which a constant and uniform temperature gradient may be maintained. the coating composition to be measured is spread uniformly in one of several sample wells. The point at which the film becomes discontinuous when dry is observed and this temperature is recorded as the minimum film formation temperature (MFT). to ensure that the films are actually continuous when formed above the MFT, the films are scraped with a knife edge moving in the direction from low to high temperature. Below the MFT the material chips off the bar easily but above the MFT the coating does not lift off the bar. The transition between easily chipped to strong coating takes place at the MFT.

The minimum film formation temperature of a polymeric blend is not, however, what might be expected from a weighted average of the minimum film formation temperatures of each polymeric component in the blend. The present inventor has found that the minimum film formation temperature of a polymeric blend is determined principally by the minimum film formation temperature of the polymer which acts as the continuous phase in the blend. Thus it was postulated that if the continuous phase of the polymer blend is composed of a relatively soft polymer, then it might be possible to achieve the desired physical properties of the final coating whilst still obtaining a relatively low minimum film formation temperature by blending that polymer, as the continuous phase, with a smaller amount of a relatively harder polymer, as the dispersed phase, thereby eliminating the need for a coalescent.

To confirm this hypothesis two variables for evaluating the effectiveness of emulsion polymer blends useful as aqueous coating binders were selected: minimum film formation temperature and block resistance. Blocking refers to the tendency of painted surfaces to stick together when placed in contact with each other under pressure. It is important for an interior paint to have good resistance to blocking (block resistance) especially when painted surfaces of doors and windows come into contact. The block resistance of a paint depends on the polymer's hardness and external factors such as pressure, temperature, humidity and drying conditions such as for example, air flow. Block resistance is tested by placing two painted surfaces in contact with each other (either stacked or face to face) under a fixed pressure for a given time and temperature. The two surfaces are then separated and their surface appearance is visually rated for their resistance to being stuck together from a worst case (1) to best case (10). By varying the composition and relative weight concentrations of the continuous phase polymer and the dispersed phase polymer the inventor has been able to form polymer blends which could be applied at low temperatures while at the same time obtaining desirable film properties without the need for a coalescent. In addition to eliminating the need for a coalescent, it has been found that the emulsion polymers can be simply blended together without phase separation occuring in the final film. This result demonstrates the versatility of the invention.

It has been found that if a soft emulsion polymer is blended with increasing amounts of a hard emulsion polymer, the MFT of the blend will remain about equal to the MFT of the soft polymer until the hard polymer is about 50% of the polymer blend. Below 50 weight percent hard polymer the soft polymer is the continuous phase and the hard polymer is the dispersed phase. Above 50 weight percent hard polymer, the hard polymer becomes the continuous phase and the soft polymer becomes the dispersed phase, and the MFT of the polymer blend begins to increase rapidly as more hard polymer is added until the MFT of the blend is equal to the MFT of the hard polymer.

In the practice of the invention the relative weight percentages of the soft polymer and hard polymer in the polymer blend range from about 20 to about 60 weight percent hard polymer to from about 80 to about 40 weight

percent soft polymer. Preferably the weight percentage of hard polymer to soft polymer is in the range of from about 20 to about 40 weight percent hard polymer and from about 80 to about 60 weight percent soft polymer.

The polymer blend of the invention must contain at least one soft polymer and at least one hard polymer. The polymers may be homopolymers or copolymers. The polymers are preferably prepared by conventional aqueous emulsion polymerization techniques well known in the art. The polymers used in the illustrative examples which follow were prepared by a gradual addition emulsion polymerization technique, using an anionic surfactant, to control the particle size, stability and performance of the polymers. Suitable anionic surfactants useful in the process include for example: sulfates of fatty alcohols, such as for example lauryl sulfate; sulfation products of oxylated alkylphenols, preferably oxyethylated alkylphenols where the alkyl group contains 8 to 12 carbon atoms such as for example octylphenol, nonyl phenol and dodecyl phenol; water soluble alkali metal salts of fatty acids, such as for example sodium stearate and sodium oleate; and sulfonated and alkylated biphenyl ethers. Ureido-functional monomers, as described in US-A-4,777,265 and references cited therein, are also preferably employed. Buffers for pH control, and post polymerization addition of initiator to remove residual unreacted monomers may also be preferably employed.

The term "soft" polymer and the term "hard" polymer are used herein in a relative fashion to differentiate between the two polymers. The specific degree to which the soft polymer is "soft" and the hard polymer is "hard" is determined by the calculated T_g's of the polymers.

The soft polymer should have a T_g such that the polymer will form a film when applied to a substrate. Preferably the T_g should be between minus 20 degrees Centigrade and room temperature, 20 degrees Centigrade, preferably below 15°C. More preferably the soft polymer should have a T_g between minus 5 degrees Centigrade and 10 degrees Centigrade, and most preferably from 0 degrees Centigrade to 5 degrees Centigrade.

The hard polymer is required to be present in the blend to provide the film with the desired physical properties, such as for example hardness and block resistance. The T_g of the hard polymer should be greater than room temperature (20°C), preferably greater than 25 degrees Centigrade, and most preferably in the range 25 to 65 degrees Centigrade.

The T_g of the soft polymer and hard polymer can be approximated from the published T_g values of the constituent monomers using, in the case of copolymers, the Fox equation ($1/T_g$ copolymer = $1/T_g$ monomer A + $1/Tg$ monomer B+$1/Tg$ monomer n [(etc.]). More accurately, the Tg 's can be measured using Differential Scanning Calorimetry.

One or more of the monomers used to form the soft polymer may have a T_g in excess of the calculated T_g of the copolymer, and likewise one or more of the monomers used to form the hard polymer may have a T_g less than the calculated T_g of the hard polymer, provided that the overall T_gs of the soft polymer and the hard polymer are within the ranges set forth above.

When the soft polymer and the hard polymer are copolymers they may be prepared using some of the same monomers but in different proportions depending upon the T_gs of each monomer. The polymers are prepared from conventional ethylenically unsaturated monomers typically used in the preparation of polymeric latex binders for use in coatings. These monomers include, for example, lower alkyl (C_1-C_{10}) acrylates, lower alkyl (C_1-C_{10}) methacrylates, styrene, alpha-methyl styrene, other substituted styrenes, ethylene, isoprene, butadiene, vinyl chloride, vinylidene chloride, acrylonitrile, vinyl acetate, acrylic and methacrylic acid, and the like. The polymers may additionally be formed using monomers known to increase the adhesion of the polymer to substrate surfaces, also known in the art as adhesion promoters, such as for example ureido functional monomers.

It has been found that the polymer blend of the invention may be prepared from soft and hard copolymers formed from the same monomers but in different weight ratios.

More particularly, when the soft polymer is a copolymer formed from butyl acrylate and styrene or from butyl acrylate and methylmethacrylate, having a T_g on the order of about 0-6 degrees C., the hardness and block resistance of a film prepared therefrom can be substantially increased by the blending of such soft polymers with about 40 weight percent of a hard polymer, having a T_g of 20 to 60 degrees C., formed from butyl acrylate and methylmethacrylate or butyl acrylate and styrene or from ethylhexyl acrylate, styrene and acrylonitrile.

It has also been found that the physical properties of the coating prepared from the polymer blend of the invention, such as for example block resistance, can be improved using the same concentration of hard polymer, or maintained using a lower concentration of the hard polymer, if the particle size difference between the soft polymer and the hard polymer is maximized as disclosed in US-A-3356627. Preferably the particle size of the soft polymer should be at least 300nm greater than that of the hard polymer. For example, in the case of butyl acrylate/ methyl methacrylate copolymers used as both the soft polymer and the hard polymer, the block resistance of the coating using 20% hard polymer can be improved if the average particle size of the soft polymer is relatively large, such as for example, having a diameter of about 530 nm and the average particle size of the hard polymer is relatively small, such as for example having a diameter of about 120 nm as compared with the results obtained when the average particle size of both polymers is the same, such as for example when their

diameters are both about 120 nm.

The preferred composition of the polymer blend of the invention comprises 60 weight percent soft polymer having a T_g of 4 degrees C. and 40 weight percent hard polymer having a T_g of 64 degrees C., with both soft polymer and hard polymer being formed from butyl acrylate, styrene, methacrylic acid and methyl methacrylate.

The following examples are presented to illustrate the invention. Variations on these examples within the scope of the invention are believed to be obvious to one of ordinary skill in the art.

EXAMPLE 1: Preparation of hard and soft emulsion polymers.

The polymers used in the examples which follow were prepared by a standard emulsion polymerization processes as described herein.

BA/MMA or BA/ST/MMA polymers

To a 5 litre stirred reactor was added 1000 grams (g) deionized water (DI water) and 2.5g of an anionic surfactant. To the stirred mixture at 85°C was added 92 g of Monomer Emulsion (ME), an initial charge of ammonium persulfate initiator in 100 g DI water, followed by adding sodium carbonate in 100 g DI water, in the amounts indicated below in Table 1. The remainder of the ME was added gradually over 3.5 hours along with a solution of ammonium persulfate in 150 g DI water (cofeed), while temperature was maintained between 80° and 85° C for another half hour. The final reaction mixture was cooled while additional initiator was added to remove residual monomers and then neutralized to pH 7 with 28% aqueous ammonia. A biocide solution was then added. Variations in the composition of the polymer samples and ingredients used in the process are shown in Table 1.

TABLE 1

	Sample Number			
Ingredients (grams)	1	2	3	4
Monomer Emulsion				
DI Water	460	460	460	460
Anionic Surfactant	18.7	18.7	18.7	18.7
Butyl acrylate (BA)	1105	459	969	459

Methyl methacrylate (MMA)	39.1	19.5	680	1190
Styrene (St)	496.4	1179	0	0
Adhesion promoter	17	8.5	17	17
Methacrylic acid (MAA)	42.5	34	34	34
<u>Other Ingredients</u>				
Ammonium persulfate (initial)	7.3	6.8	2.6	2.6
Sodium carbonate	4.25	4.25	1.7	1.7
Ammonium persulfate (cofeed)	2.9	1.7	1.7	1.7
<u>Physical Properties of Polymers</u>				
Viscosity (cps)	40	25	30	23
% Solids	43.6	43.3	44.4	44.54
Particle size (nanometers)	119	122	136	135
<u>Overall Composition</u>				
BA/ST/MAA/MMA	65/29.2/2.5/2.3	27/69.4/2/1.1	57/0/40/2	27/0/2/70

A similar process was used to prepare 2-ethyl hexyl acrylate/styrene and 2-ethyl hexyl acrylate/styrene/acrylonitrile polymer samples as described below.

<u>Sample 5: EHA/ST/AN Polymer (30 EHA/40 St/25 AN)</u>

A monomer emulsion was prepared from 460 g DI water, 18.7 g anionic surfactant, 39.3 g methyl methacrylate, 695.3 g styrene (ST), 34 g methacrylic acid (MAA), 510 g 2-ethyl hexyl acrylate (EHA), 425 g acrylonitrile (AN), and 34 g of an ureido-containing adhesion promoting monomer. To a five litre stirred reactor was added 1400 grams DI water and 2.5 g of an anionic surfactant. To the stirred mixture at 85 ° C was added 92 g of the monomer emulsion, 2.6 g ammonium persulfate in 50 g DI water and 1.7 g sodium carbonate in 100 g DI water. The remainder of the monomer emulsion was added gradually over 3 hours along with a solution of ammonium persulfate in 150 g DI water while maintaining the temperature between 80 and 85 °C. The final reaction mixture was cooled, residual monomer removed, and neutralized to pH 7 with 28% aqueous ammonia. The emulsion polymer obtained was 41.5% solids, had an average particle size of 121 nm and a Brookfield viscosity of 22 cps.

<u>Sample 6: EHA/ST/AN Polymer (50 EHA/19ST/25 AN)</u>

A monomer emulsion was prepared from 460 grams DI water, 18.7 g anionic surfactant, 39.3 g methyl methacrylate, 350.2 g styrene, 34 g methacrylic acid, 855.1 g 2-ethyl hexylacrylate, 425 g acrylonitrile (AN) and 34 g of a ureido-containing adhesion promoting monomer. To a five litre stirred reactor was added 1400 g DI water and 2.5 g of an anionic surfactant. To the stirred mixture at 85° C was added 92 g of the monomer emulsion, 2.6 g ammonium persulfate in 50 g DI water, and 1.7 g sodium carbonate in 100 g DI water. The remainder of the monomer emulsion was added gradually over 3 hours along with a solution of ammonium persulfate in 150 g DI water while maintaining the temperature between 80 to 85 ° C. The final reaction mixture was cooled, residual monomer removed, and neutralized to pH 7 with 28% aqueous ammonia. The emulsion polymer obtained was 40.5% solids, had a particle size of 121 nm and a Brookfield viscosity of 20 cps.

<u>Sample 7: BA/ST polymers (57 BA/38 ST)</u>

A monomer emulsion was prepared from 460 g DI water, 18.7 g anionic surfactant, 39.3 g methyl methacrylate, 640.9 g styrene, 34 g methacrylic acid, 969 g butyl acrylate, and 16.8 g of a ureido-functional adhesion promoting monomer. To a 5 litre stirred reactor was added 1400 g DI water, and 2.5 g of an anionic surfactant.

To the stirred reactor at 82 °C was added 92 g of the monomer emulsion, 2.6 g ammonium persulfate in 50 g deionized water and 1.7 g sodium carbonate in 50 g deionized water. The remainder of the monomer emulsion was added to the reactor over 3.5 hours along with a solution of 1.7 g ammonium persulfate in 150 g DI water while the temperature was maintained between 80 to 85 °C. The final reaction mixture was cooled and neutralized to pH 7 with 20% aqueous ammonia. The emulsion polymer obtained was 41.3% solids, 111 nm average particle size diameter, and had a Brookfield viscosity of 22 cps.

This process was also employed to prepare two other BA/ST emulsion polymers having the composition 61 BA/34 ST and 61 BA/36 ST, respectively. These polymers were evaluated and are identified by their overall composition in the following application example.

Sample 8: BA/ST (48 BA/47 ST)

A monomer emulsion was prepared from 460 g DI water, 18.7 g anionic surfactant, 39.3 g methyl methacrylate, 793.9 g styrene, 34 g methacrylic acid, 816 g butyl acrylate and 16.8 g ureido-functional adhesion promoting monomer. To a five litre stirred reactor was added 1400 g DI water and 2.5 g anionic surfactant. To the stirred reactor at 82 ° C was added 92 g of the monomer emulsion, 2.6 g ammonium persuflate in 50 g DI water, and 1.7 g sodium carbonate in 50 g DI water. The remainder of the monomer emulsion was added over 3.5 hours along with a solution of 1.7 g ammonium persulfate in 150 g DI water while the temperature was maintained between 80 and 85 °C. The final reaction mixture was cooled and neutralized to pH 7 with 28% aqueous ammonia. The emulsion polymer was 40.7% solids, had an average particle size diameter of 110 nm and a Brookfield viscosity of 20 cps.

Example 2 Paint Formulation

The hard/soft polymer blends of the invention were evaluated (as shown in the examples which follow) in a standard paint formulation having the following composition. (1 lb = 2.2 kg, 1 gallon = 4.54 l).

TABLE 2

Material	Material Type	lb	gal.
1,2 Propanediol	Solvent	72.00	8.32
Sodium Salt of Polymeric Carboxylic Acid (35%) in H_2O	Dispersant	13.63	1.48
Petroleum Derivatives & Additives	Defoamer	1.00	0.13
Rutile Titanium Dioxide	Pigment	267.64	8.03
Water		30.00	3.60
Latex Blend		531.99	61.98

(as identified below)			
Dioctyl Sodium Sulfosuccinate (75%) in Ethanol and H_2O	Surfactant	1.71	0.21
Water		10.00	1.20
50% Aqueous Solution of non-metallic organic compound	Biocide	2.00	0.21
Petroleum Derivatives & Additives	Defoamer	1.00	0.13
Polyurethane Resin (20%) in diethyleneglycol monobutyl ether (10%) and H_2O(70%)	Thickener	32.60	3.91
Water		90.00	10.80
		1053.57	100.00

Pigment Volume Concentration = 23.65%
Volume Solids = 33.95%

Example 3

This example demonstrates the effect of composition, hardness and polymer blend ratios on the properties of the polymer blends formed by mixing the emulsion polymer samples prepared according to Example 1.

The data presented in Table 4 shows that soft BA/ST and BA/MMA latexes (MFT = 0-6) have low hardness and poor block resistance; however, by blending in approximately 40% of a hard latex (MFT = 60), whether BA/ST or 2-ethyl hexyl acrylate (EHA)/ST/ acrylonitrile (AN), block resistance and hardness are upgraded, and MFT does not significantly increase. This holds true whether the soft phase is BA/ST or BA/MMA.

TABLE 4

			Blend MFT°C	Block 1 Day RT	Resistance 7 Day/ 100°F	Tukon Hardness (1 wk.dry) KHN	Low Temp. Film Formation Cracking Over Bare Pine @46°F
I. Soft Phase -MFT °C							
Sample 7	6						
Sample 3	1						
II. Blends with 57 BA/28 ST							
Hard Phase	MFT°C	Soft/hard Ratio					
Sample 6	22	80/20	7.8	3+/0	0/0	1.0	none
Sample 6	22	60/40	7.1	3/3	2/3	1.2	trace
Sample 5	59	80/20	7.3	2/1	1/2	1.0	none
Sample 5	59	60/40	6.2	9+/9	8/8	1.9	v-slt
Sample 8	19	80/20	7.3	0/0	0/0	1.0	trace
Sample 8	19	60/40	7.3	1/0	0/0	1.2	slight
Sample 2	61	80/20	7.8	2/3	3/3	1.2	trace
Sample 2	61	60/40	9.35	8+/9	9/9	2.7	mod-hvy
III. Blends with Sample 3							
Sample 6	22	80/20	1.6	1/1	1/2	1.0	none
Sample 6	22	60/40	5.7	2/3	1/1	1.2	none
Sample 5	59	80/20	2.3	1/2	3/3	1.3	none
Sample 5	59	60/40	6.0	8/8	8+/9	2.0	none
Sample 8	19	80/20	1.5	0/0	0/0	1.1	none
Sample 8	19	60/40	3.6	1/1	1/2	1.2	none
Sample 2	61	80/20	1.8	0/2	3/3	1.1	none
Sample 2	61	60/40	6.1	9/10	9+/9	2.3	none
IV. Control[1]	35			9/8+	6+/6+	1.6	slight

Control polymer had the composition: 10 EA/ 35 BA/ 48.8 ST/3.7 MMA/2 MMA/ 0.5 ureido functional mono

BA	=	Butylacrylate	EHA	=	2-ethlhexylacrylate
St	=	Styrene	AN	=	acrylonitrile
MMA	=	Methylmethacrylate			

Example 4

This example demonstrates that blends containing a minimum amount of 30% of T_g= 63 hard phase are needed for the block resistance to begin to improve. At 40% hard phase, block resistance is good. In addition the BA/St blends containing a soft phase with a T_g = 15 showed heavy cracking in the low temperature film formation test, but no cracking was observed when using a T_g = 4 soft phase. A T_g = 9 soft phase gave intermediate results. BA/MMA blends gave good film formation (no cracking) when the phase had a T_g of 10.

TABLE 5

Effect of Soft Phase TG and Blend Ratios on Blend Properties Comparison of BA/ST VS. BA/MMA

Composition	T_g1	Block Resistance 1 Day RT	Block Resistance 7 Day/ 100°F(38°C)	Low Temp. Film Formation Cracking Over Bare Pine @ 46°F (8°C)
I. Soft Phase				
Sample 7	14.9	0/0	0/0	None
61 BA/34 St	8.8	0/0	0/0	None
Sample 1	4.3	0/0	0/0	None
Sample 3	10.8	0/0	0/0	None
61 BA/36 MMA	1.8	0/0	0/0	None
II. Cold Blends with Hard BA/St2 (MFT = 60°C/TG = 63.7°				
Soft Phase	Soft/Hard Ratio			
Sample 7	70/30	3+/3+	3+/3+	heavy
Sample 7	65/35	8+/8	4/6	heavy
Sample 7	60/40	8+/9	9/9	heavy
61 BA/34 St	60/40	8/8+	8+/8+	slight
Sample 1	70/30	3/3	3+/4	none
Sample 1	65/35	4+/4+	4+/5	none
Sample 1	60/40	8/8+	6/7	none
III. Cold Blends with Hard BA/MMA3 (MFT = 60°C/T_g = 60.4°)				
Sample 3	60/40	8+/8	9/9	none
61 BA/36 MMA	60/40	9/9	9/9	none
IV. Control4		4+/5	5/5	mod-hvy
Control5		4/4	4+/5	sl-mod

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1 DSC Inflection °C

2 Sample 2

3 Sample 4

4 Control polymer had the composition: 10 EA/ 35 BA/ 48.8 ST/ 3.7 MMA/2 MAA/ 0.5 ureido functional monomer

5 Control was a blend of two polymers: polymer 1 (96% of blend) was 57 EA/41.7 MMA/ 1.3 MAA polymer 2(4%) was 43.4 BA/51.1 MMA/2 AA/3.5 ureido functional monomer.

Claims

1. A film forming polymeric binder comprising a blend of at least one hard emulsion polymer having a glass transition temperature (T_g) greater than 20°C, preferably from 25 to 65°C, and at least one soft emulsion polymer having a T_g less than 20°C, preferably from 10°C to -5°C, wherein said blend comprises from 20 to 60, preferably from 20 to 40 weight percent of said hard emulsion polymer and from 80 to 40, preferably from 80 to 60 weight percent of said soft emulsion polymer.

2. Binder according to claim 1 wherein said hard emulsion polymer is a copolymer formed from butyl acrylate, styrene, methacrylic acid, methyl methacrylate, 2-ethylhexyl acrylate and/or acrylonitrile.

3. Binder according to claim 1 or 2 wherein said soft emulsion polymer is a copolymer formed from butyl acry-

late, styrene, methacrylic acid, and/or methyl methacrylate.

4. Binder according to any preceding claim wherein said soft emulsion polymer comprises 60 weight percent of the blend and has a T_g of 5°C, and said hard emulsion polymer comprises 40 weight percent of the blend and has a T_g of 65°C, both the soft polymer and the hard polymer being copolymers formed from butyl acrylate, styrene, methacrylic acid and/or methyl methacrylate.

5. Binder according to any preceding claim wherein the hard emulsion polymer and soft emulsion polymer are each copolymers formed from the same monomers.

6. Binder according to claim 5 wherein said hard and soft emulsion polymers each comprise a copolymer formed from butyl acrylate and methyl methacrylate monomers.

7. Binder according to any preceding claim wherein the difference between the average particle size diameter of the soft emulsion polymer and said hard emulsion polymer is maximized, preferably such that the particle size of the soft polymer is at least 300 nm greater than that of the hard polymer.

8. Binder according to claim 7 where the average particle size diameter of said soft emulsion polymer is about 530 nm and the average particle size diameter of said hard emulsion polymer is about 120 nm.

9. An aqueous coating composition containing a film forming polymeric binder according to any preceding claim.

10. An aqueous coating composition according to claim 9 free of volatile organic solvent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 6114

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 9, no. 82 (C-275)(1805) April 11, 1985 & JP-A-59 215 365 (NIHON AKURIRU KAGAKU K.K.) * abstract *	1,9	C09D133/02 C09D133/06 C09D125/14
X	EP-A-64 228 (BASF AG) * claims; examples 1-2 *	1,3	
A	US-A-4 826 907 (K. MURAO ET AL.) * claims 1,3,7-8; examples; table 1 *	1-3,5,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 OCTOBER 1991	FUHR C.K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document